The University of Chicago

A STUDY OF THE ALKALI AND ALKALINE EARTH METAL DIHYDROGEN ARSENIDES

A DISSERTATION SUBMITTED TO THE FACULTY
OF THE DIVISION OF THE PHYSICAL SCIENCES
IN CANDIDACY FOR THE DEGREE OF DOCTOR
OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY
JUNE, 1941

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ALFRED BAYES

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INTRODUCTION

Arsine, unlike ammonia, does not react in the liquid state with the alkali metals to form compounds analagous to the alkali metal amides.[1] Lebeau observed only the formation of a brown coating on sodium or potassium when these metals were treated with arsine in sealed tubes either at -80° C. or at room temperature. Accompanying the formation of the brown reaction product, there was a simultaneous evolution of hydrogen. Lebeau described the brown product as an impure arsenide which always contained a little excess arsine and arsenic.

Hugot[2] prepared the compounds Na_3As, K_3As, and K_2As_4 by allowing arsenic to react with solutions of sodium and potassium amides in liquid ammonia and by then decomposing the nitrogenous products at 300° C. in vacuo. The resulting arsenides contained amide impurities and were always amorphous. Lebeau[1] modified Hugot's procedure by substituting arsine for arsenic. Arsine was bubbled slowly into liquid ammonia solutions of the alkali metals until the blue color was discharged. The remaining yellow solution when evaporated left a red product, identical with the compound described by Hugot and composed of alkali metal arsenides and ammonia. By thermal decomposition an impure amorphous arsenide was obtained. Later, Lebeau, by extending his reaction to a study of calcium arsenide, succeeded in

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[1]Lebeau, Bull. Soc. Chim. 23, 251 (1900).

[2]Hugot, Compt. Rend. 129, 603 (1899).

preparing and identifying Ca_3As_2.[1]

More recently a study was made of the reaction of arsine with solutions of potassium in liquid ammonia.[2] It was shown that the reaction may be represented by the equation:

$$AsH_3 + K \xrightarrow{\text{in } NH_3} KAsH_2 + \tfrac{1}{2}H_2$$

The validity of this equation was confirmed by:

(a). Measuring the amounts of the reactants and the volume of hydrogen evolved.

(b). Allowing the product to react with an acid in liquid ammonia and measuring the volume of arsine produced according to the equation:

$$KAsH_2 + NH_4Cl \xrightarrow{\text{in } NH_3} KCl + NH_3 + AsH_3$$

(c). Demonstrating the formation of methyl arsine (CH_3AsH_2) when the product was treated with methyl chloride in liquid ammonia.

(d). Measuring stochiometric amounts of hydrogen evolved during thermal decomposition.

Potassium dihydrogen arsenide was found to be a white, crystalline solid, readily soluble in liquid ammonia. Thermal decomposition of the compound, which readily occurred at 125° - 150° C., liberated 90 - 100% of the theoretical amount of hydrogen. Two possible mechanisms were suggested for the reaction:

(1). $xKAsH_2 \longrightarrow (KAs)_x + xH_2$

(2). $3KAsH_2 \longrightarrow K_3As + 2As + 3H_2$

The reaction of arsine with sodium in liquid ammonia apparently differs in some respects from the corresponding reaction with potassium. Lebeau, who investigated the former reaction, obtained a red reaction product rather than a white crystalline

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[1]Lebeau, Ann. Chim. Phys. 25, 470 (1902).

[2]Johnson and Pechukas, J. A. C. S. 59, 2068 (1937). Pechukas, Ph. D. Dissertation, University of Chicago (1937).

material such as the potassium compound described by Johnson and Pechukas. This apparent difference between the two compounds has been confirmed in the present investigation.

According to results obtained in the present study, sodium, lithium, and calcium dihydrogen arsenides are well-defined, white crystalline compounds considerably less stable thermally than the corresponding potassium compound. Since they are all unstable at room temperature, they must be studied at low temperatures if their true nature is to be determined. Earlier investigators undoubtedly carried out the reactions in which they are formed at temperatures too high to permit isolation of the initial products; consequently, only the neutral arsenides, the products of decomposition, were described.

DISCUSSION

The chemical properties of the hydrides of the fifth group elements vary progressively with increasing atomic weight of the central atom. Their relative stabilities appear in the following table:

TABLE 1

FREE ENERGIES OF FORMATION OF THE FIFTH GROUP HYDRIDES[1]

Compound	ΔF^o
NH_3 (g)	-3,940
PH_3 (g)	2,880
AsH_3 (g)	37,700 (may be somewhat high)
SbH_3 (g)	35,500
BiH_3 (g)	55,000

Thus, of all the hydrides in question, ammonia alone is thermodynamically stable at room temperature. The rates of decomposition of phosphine and arsine aré very slow at room temperature. The ability of the fifth group hydrides to react with metals is due to their acidic character. Ammonia has well-defined acid properties: its interaction with the alkali and alkaline earth metals gives rise to a series of stable amides. According to the data in Table 1, the metal-hydrogen bonds from ammonia to bismuthine decrease in stability; hence, the heavier hydrides might be expected to display acidic properties increasingly greater than those of ammonia. The reaction between alkali metals and ammonia

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[1]W. M. Latimer, "The Oxidation States of the Elements," Prentice Hall, Inc., New York, 1938, p. 302.

to form amides is very slow unless catalysed; but both phosphine[1] and arsine[2] react almost instantaneously with alkali metals in liquid ammonia to form amide-like compounds. Although the decreasing metal-hydrogen bond strengths of the heavier metals in the fifth group facilitate the formation of amide-like compounds, such compounds with very weak hydrogen bonds might be expected to lose hydrogen readily. Many bismuthides of the type Na_3Bi are, in fact, known[3], whereas no bismuth compound of the amide type has been reported. Thus, the formation of amide-like compounds of the fifth group elements should be favored by increasing atomic weight of the central atom, whereas the stability of such substances should decrease in the same order.

Although the above considerations suggest a reason why the alkali dihydrogen arsenides should be thermally less stable than the amides, they do not explain the observed variation in thermal stability of different members of this class. Such a variation might be expected, since the thermal stability of the corresponding amides decreases markedly from potassium to lithium.

In a series of publications, Zintl[4] has shown that for the existence of polyanionic compounds ammonation is essential; without ammonation they would undergo a transition from a salt into a purely intermetallic substance. The ammonia is supposed to surround the cation and thereby to decrease its deforming action on the negative polyanion. Now the AsH_2^- ion is not as large as a typical polyanion nor is it held together by a type

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[1]Legoux, Compt. Rend., 207, 634 (1938).

[2]Johnson and Pechukas, J. A. C. S., 59, 2068 (1937).

[3]Latimer, "The Oxidation States of the Elements," p. 112.

[4]Zintl, Z. Phys. Chem. B16, 195 (1932); B16, 183 (1932); Z. Phys. Chem. A154, 47 (1931).

of bonding usual in polyanions; however, its stability in the crystalline form might conceivably be greatly influenced by the deforming action of the cation. Thus in compounds of the arsenide ion with alkali metals possessing large ratios of charge/ionic radius, a transition from a purely salt-like compound to an intermetallic phase might well occur; hydrogen would be simultaneously evolved.

Cationic size has been shown to affect the stability of sulfur and iodine polyanions. "Only the largest alkali metals, rubidium and cesium, form triiodides. The only stable potassium and sodium compounds have the compositions KI_3-H_2O and NaI_3-$2H_2O$ respectively, and break if they are dehydrated, just as do Zintl's polyanionic salts when they are deammonated."[1]

By applying Zintl's idea to the alkali metal arsenides, the following order of decreasing stability is predicted for those compounds:

Compound	Cation radius[2]	Charge/radius (cation)[3]
$CsAsH_2$	1.69	0.61
$RbAsH_2$	1.48	0.67
$KAsH_2$	1.33	0.71
$NaAsH_2$	0.95	1.00
$Ca(AsH_2)_2$	0.99	1.90
$LiAsH_2$	0.60	--

However, this order might be effected in the crystalline state by the stabilizing action of ammonation. Lithium and sodium as well

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[1]H. J. Emeleus and J. S. Anderson, "Modern Aspects of Inorganic Chemistry," G. Routledge and Sons, London, 1938, p. 450.

[2]L. C. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, New York, 1939, p. 346.

[3]Emeleus and Anderson, "Modern Aspects of Inorganic Chemistry," p. 166.

as calcium ions do, in fact, tend more strongly to surround themselves with ammonia molecules than do potassium, rubidium, or cesium. If ammonia effectively increases the diameter of the sphere of charge distribution around alkali metal ions, it should inhibit the transition from salt-like to intermetallic bonding. In ammonia solution such a compound as $[Na^{+}(NH_3)_x]\ AsH_2^{-}$ should be completely stable and highly ionized. The yellow color of ammonia solutions containing alkali metal dihydrogen arsenides may be ascribed to the presence of AsH_2^{-} ions. In support of this idea, it may be mentioned that solutions of arsine in liquid ammonia have a yellow color which is apparently due to ionization similar to that described by Royen,[1] for phosphine solutions:

$$NH_3 + PH_3 \rightleftharpoons (NH_4)^{+}\ PH_2^{-}.$$

Since arsenic-hydrogen bonds are even weaker than phosphorous-hydrogen bonds the ionization should be greater for arsine than for phosphine:

$$NH_3 + AsH_3 \rightleftharpoons (NH_4)^{+}\ AsH_2^{-}$$

The present study is an attempt to correlate the effects of both cation size and ammonation with the stability of alkali and alkaline earth metal dihydrogen arsenides. An effort has been made to determine the nature of the thermal decomposition of these arsenides and the products resulting therefrom.

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[1]Royen, Z. fur Anorg. und Allgem. Chem. 235, 324 (1938).

EXPERIMENTAL

Preparation of Arsine

The arsine used in this investigation was prepared by two methods. According to the method of Johnson and Pechukas[1] freshly cut sodium (1-2 gr.) together with more than the theoretical quantity of powdered arsenic metal was placed in a reaction vessel into which was condensed 50-60 cc. of liquid ammonia. The mixture was allowed to stand at -33° C. for several days, during which time the following reactions presumably occurred:

$$3Na + As \longrightarrow Na_3As$$

$$Na_3As + 2As \longrightarrow Na_3As_3$$

$$Na_3As_3 + 2As \longrightarrow Na_3As_5$$

The blue sodium color in the ammonia persisted, even after an interval of several days, but a considerable amount of brick red solid formed on the walls of the flask. The system was purged with ammonia gas to remove any hydrogen that might have been formed. The volume of hydrogen thus obtained (ordinarily about 50-75 cc.) indicated a very small loss of sodium due to amide formation. Addition of a little ammonium chloride rapidly discharged the blue color of the unreacted sodium, leaving a clear reddish-orange liquid and a residue of white crystalline material mixed with excess arsenic. Further addition of ammonium chloride resulted in the evolution of arsine and simultaneous deposition of black, finely-divided arsenic which gave the entire solution a dark brown muddy appearance. The equations[2] describing the

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[1] Johnson and Pechukas, J. A. C. S., 59, 2065 (1937).

[2] Ibid.

reactions with ammonium chloride are;

$$Na_3As + 3NH_4Cl \longrightarrow 3NaCl + AsH_3 + 3NH_3$$

$$Na_3As_3 + 3NH_4Cl \longrightarrow 3NaCl + AsH_3 + 3NH_3 + 2As$$

If all of the hydrogen was removed from the system before the addition of ammonium chloride the gaseous product formed when the ammonium chloride was added was very nearly pure arsine. This gas was collected over dilute sulfuric acid and dried by passage through barium oxide - phosphorous pentoxide drying columns; it was then freed from hydrogen by freezing the arsine at liquid nitrogen temperature and pumping off non-condensible gases. Molecular weight determinations agreed with the theoretical value within the limit of experimental error. Yields varied from 25 to 50% of the theoretical value, based on the amount of sodium used. Since considerable amount of arsine is lost because of its solubility in the dilute sulfuric acid of the scrubbing tower, the true arsine yield of the reaction is much higher than the amounts actually obtained.

The second method used for the preparation of arsine consisted of the hydrolytic decomposition of a commercial grade of magnesium arsenide. A weighed quantity of this material was placed in a reaction flask and subjected to dropwise addition of freshly boiled distilled water. Evolved gases were collected and analyzed according to two procedures;

(1). The gases were swept through the system by a slow current of ammonia gas and collected over dilute sulfuric acid in a scrubbing tower. The gas mixture was then dried over phosphorous pentoxide and a separation of hydrogen from the condensible gases was effected in the usual manner.

(2). Due to the solubility of arsine in aqueous solutions

it was found desirable to avoid collection of the gases over water. Accordingly the evolved gases were allowed to expand through a phosphorous pentoxide drying tube into a large evacuated reservoir. The condensible and non-condensible gases could then be separated in a liquid nitrogen-cooled trap.

Table 2 contains the results obtained in the preparation of arsine from the hydrolytic decomposition of magnesium arsenide.

TABLE 2

PREPARATION OF ARSINE BY HYDROLYTIC DECOMPOSITION OF MAGNESIUM ARSENIDE

Exper.	Wt. Mg_3As_2	Vol. AsH_3 Exper.	Evolved Theor.	Per cent Yield AsH_3	Vol. H_2 Evolved
1.'	0.5720 gm.	23cc.	110cc.	21.0	9cc.
2.'	2.2020 gm.	196cc.	425cc.	46.0	36cc.
3."	1.6455 gm.	302cc.	345cc.	87.5	29.3cc.
4."	0.5575 gm.	109cc.	118cc.	92.0	4.8cc.
5."	0.7985 gm.	149cc.	168cc.	89.0	6.8cc.

'Evolved gases treated according to procedure (1).
"Procedure (2) used in these experiments.

The low yields of arsine obtained in experiments (1) and (2) indicate the solubility losses that may be expected when the gases are collected over water. Theoretical values in Table 2 are based on the reaction:

$$Mg_3As_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + 2AsH_3$$

Hydrogen evolved during the experiments was due to impurities in the magnesium arsenide or to slight dissociation of arsine caused by heat liberated in the reaction. Decomposition of magnesium arsenide by means of dilute sulfuric acid did not increase the yields above those obtained when pure water was used. Molecular weights determined for samples of the condensible gases agreed with the theoretical value for arsine within the limits of experimental error.

Reaction of Arsine with Solutions of Sodium in Liquid Ammonia

The following procedure was used in carrying out reactions between arsine and sodium in liquid ammonia. Sodium samples were cut and weighed under a protective coating of mineral oil, then washed in petroleum ether and introduced into a weighed reaction flask. The flask after being sealed on to the vacuum system, was evacuated and immersed in a carbon dioxide-acetone bath. Ammonia gas was next introduced until approximately 10 cc. of liquid had condensed. By means of a calibrated Toepler pump, arsine was then bubbled slowly into the flask until the blue color of free sodium was discharged. The end point of the reaction was always sharply defined by a color change from an intense blue to a yellow or greenish-yellow.

Calculations of the molar ratios of the reactants were based on the weight of sodium used. The amount of arsine was determined directly by measuring the volumes delivered from the Toepler pump. After the preparation had been terminated by evaporating the solvent, the gases were collected over dilute sulfuric acid solution which dissolved the ammonia and thus permitted the amount of hydrogen evolved in the reaction to be determined.

Typical results obtained by carrying out the reaction between arsine and solutions of sodium in liquid ammonia are recorded in Table 3.

According to the results below, the arsine used up is sometimes less than the theoretical amount. This fact indicates either an incomplete reaction or the establishment of an equilibrium between sodamide and sodium dihydrogen arsenide. Whereas the volume of reacting arsine used is sometimes low, the quantity of hydrogen evolved is always greater than that calculated from

the equation:

$$AsH_3 + Na \longrightarrow NaAsH_2 + \frac{1}{2}H_2$$

TABLE 3

PREPARATION OF SODIUM DIHYDROGEN ARSENIDE

Exper.	Moles Sodium	Moles Arsine	Moles H_2 (evolved)	Molar Ratio
1.	.00604	.0067	.0032	1.0 : 1.10 :0.53
2.	.00486	.00468	.00267	1.0 : 0.96 :0.55
3.	.00432	.00402	.00241	1.0 : 0.93 :0.56
4.	.00206	.00184	.0012	1.0 : 0.89 :0.58
			(Theoretical)	1.0 : 1.00 :0.50

After completion of the reaction, there remained a perfectly clear yellow solution and a very small trace of white insoluble residue which may well have been sodamide. When the reaction flask was warmed to boil off the solvent, the solution always changed from bright yellow to deep red when about one half of the ammonia had been removed. Presumably, after the solvent had evaporated at room temperature, there remained in the reaction flask, a product with composition corresponding to $NaAsH_2$, or a stable ammonate thereof. Actually, in all experiments carried out in the manner described, there was obtained a non-homogeneous red product which comprised both a liquid and a solid phase and which appeared to be stable at room temperature. The liquid phase may have consisted of extensively ammonated material or of salts dissolved in liquid ammonia; some information on this point should have been obtainable by pumping off the vapor phase and observing the vapor pressures.

At room temperature, however, such measurements gave no intelligible results. Undoubtedly, if an ammonate exists under conditions described, its dissociation pressure is greater than one atmosphere, for when the material was allowed to stand several

days the pressure slowly increased to more than 800 mm. After complete removal of ammonia a brownish-black residue remained in the flask. Numerous attempts were made, both at room temperature and at 0° C., to detect the existence of ammonates by adding known amounts of ammonia to the system and observing the volume of gas taken up; but all these efforts were unsuccessful. The brownish-black residue changed to red when ammonia was added, but the volume of ammonia required to effect this change was immeasurably small.

When the solvent is evaporated after the interaction of arsine and sodium in liquid ammonia, the residue left is undoubtedly a saturated liquid ammonia solution of either sodium dihydrogen arsenide or some decomposition product thereof. An experiment was designed to determine the amount of ammonia in this residue, and to indicate, if possible, whether or not this ammonia was combined in a definite ammonate. After the preparation had been carried out in the usual manner, the temperature of the reaction flask was brought to 0° C. as soon as evaporation of the solvent permitted. The resulting product was bright red; the liquid phase was somewhat smaller than in similar preparations carried out at room temperature.

Since the weight and volume of the flask were determined before the experiment, since a known amount of sodium and arsine were added, and since the evolved hydrogen was measured, it was possible to determine the weight of the two-phase residue as follows:

a = observed weight of material

b = weight of ammonia as calculated from volume of flask and pressure at 0° C.

c = weight of residue = a - b

The weight of the $NaAsH_2$ in this residue is the sum of the weights of sodium and arsine used, diminished by the weight of the hydrogen evolved. The weight of the ammonia in the residue is c - d.

In this experiment the values were as follows: a = 0.6471, b = 0.0896, c = 0.5575, d = 0.4081, and c - d = 0.1494 gm. Thus the ammonia associated with the residue amounts to approximately 0.0088 moles. Since 0.0043 moles of sodium dihydrogen arsenide should be present it is evident that maximum ammonation would be $NaAsH_2$-$2NH_3$.

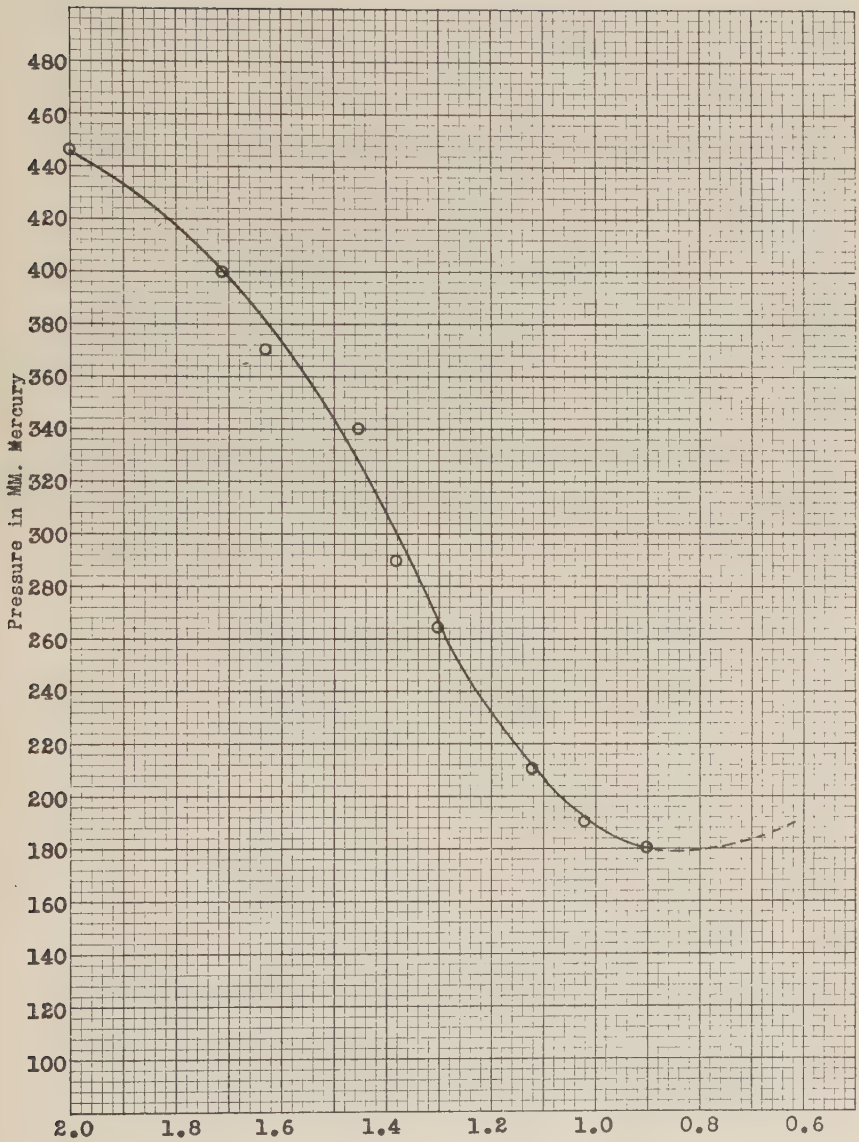
In order to investigate material corresponding in weight to sodium dihydrogen arsenide di-ammonate, the reaction flask was replaced on the vacuum system and cooled to 0° C. At this temperature vapor pressure measurements were made after the withdrawal of successive portions of NH_3. Table 4 contains the numerical results; Fig. 1 is a graphic representation of the data.

TABLE 4

VAPOR PRESSURE VS. COMPOSITION OF THE SYSTEM $NaAsH_2$ - NH_3 AT 0° C.

Moles of Bound Ammonia	Equilibrium Pressure
2.00	445
1.71	400
1.63	370
1.45	340
1.38	287
1.31	265
1.24	246
1.12	211
1.06	197
1.02	189
.90	178
(from this point on the pressure began to increase with time)	

After approximately 50% of the available ammonia had been removed from the system, the time required to attain equilibrium was increased considerably. Fig. 1 shows that at this point the



Moles of bound ammonia

Fig. 1

pressure in the reaction flask tended to increase slowly, thus making further measurements nearly valueless. This pressure increase may be due to slow decomposition of sodium dihydrogen arsenide with evolution of hydrogen.

Very little information can be obtained from the above data concerning the degree of ammonation of sodium dihydrogen arsenide. The general shape of the curve in Fig. 1 suggests an unsaturated solution of the arsenide in ammonia, but it would be difficult to explain the presence of a solid phase under such a solution. However, the fact that the curve breaks and even tends to rise at a molar composition of about one to one is very interesting.

In an experiment similar to the one described, molecular weight determinations were made on each sample of gas withdrawn. Data obtained from this experiment are given in Table 5.

TABLE 5

MOLECULAR WEIGHTS OF GASES WITHDRAWN FROM THE SYSTEM: $NaAsH_2$-NH_3 AT 0° C.

Moles of Ammonia Per Mole of Arsenide	Mol. Wt. of Gas Phase
1.65	17.4
1.38	17.0
1.00	17.0
0.60	12.9
0.40	12.7

The results indicate that sodium dihydrogen arsenide is probably stable in the presence of at least one mole of ammonia; when this last mole is removed the compound decomposes with evolution of hydrogen. The ammonia concentrations given in Table 5 are based upon weight measurements and are at best only approximate.

Since the effort to determine the degree of ammonation

of sodium dihydrogen arsenide at room temperature or at 0° C. proved unsuccessful, it was decided to carry out the measurements at lower temperatures and to determine the ammonia concentration volumetrically. The procedure was changed in the following respects:

(1). The reaction was carried out in a known amount of solvent, delivered as a gas into the reaction flask by means of a Toepler pump. Ordinarily 3 to 4 liters of gaseous ammonia were employed.

(2). The volume of hydrogen evolved in the reaction was determined by immersing the reaction flask in a liquid nitrogen bath and measuring the pressure of non-condensible gas. From the previously determined volume of the system the amount of hydrogen was calculated.

(3). The reactions were carried out at -80° C. and the flask was maintained constantly at a temperature low enough to avoid decomposition of the product. A chloroform bath at -65° C. proved convenient for vapor pressure measurements. Known quantities of ammonia were removed from the system by expanding the gas into an adjoining calibrated reservoir, which was then closed off and evacuated.

(4). The composition of the ammonates, as determined from the original volume of ammonia, was checked by comparison with the amount of withdrawal required to remove the ammonia completely from a mixture corresponding to a definite point on the composition-vapor pressure curve.

The results obtained by carrying out the reaction in the manner described are given in Table 6.

The data in this table show that the volume of hydrogen

evolved was slightly less than the theoretical amount whereas in previous preparations it was usually greater. The solutions obtained resembled those previously described. Ammonia was removed from the system, while the reaction flask was immersed in either a carbon dioxide - acetone or a chloroform bath; a yellow solid separated from the liquid phase. As soon as the last trace of the liquid had been removed, the solid phase lost its yellow color, and remained as a white crystalline material. Vapor pressure curves showed this white solid to correspond in composition to $NaAsH_2$-$5NH_3$. As more ammonia was withdrawn from the system, a pressure drop occurred at a composition corresponding to $NaAsH_2$-$4NH_3$; there is consequently an equilibrium along the constant pressure plateau between the penta- and tetra-ammonates.

$$NaAsH_2\text{-}5NH_3 \rightleftharpoons NaAsH_2\text{-}4NH_3 + NH_3$$

These two ammonates as well as the ammonia free salt resemble the corresponding potassium compounds in appearance, but when warmed to room temperature they rapidly change irreversibly into dark-colored substances. Fig. 2 shows the vapor pressure-composition curve for the system $NaAsH_2$-NH_3 at -65° C.

TABLE 6

THE PREPARATION OF SODIUM DIHYDROGEN ARSENIDE AT LOW TEMPERATURES

Trial	Moles of Sodium	Moles of Arsine	Moles of H_2 (evolved)	Molar Ratio
Theor.	1.00000	1.00000	.50000	1:1.00 :0.50
1.	.00679	.00694	.00316	1:1.02 :0.45
2.	.00378	.00380	.00173	1:1.00 :0.47
3.	.00533	.00585	.00254	1:1.09 :0.48

During the withdrawal of ammonia from the system, (which was held at -65° C.), numerous tests for hydrogen were made by condensing samples of the gas in a liquid nitrogen bath. No hydrogen was found, and the white solid product suffered no apparent decomposition at -65° C. even after the ammonia had been completely removed.

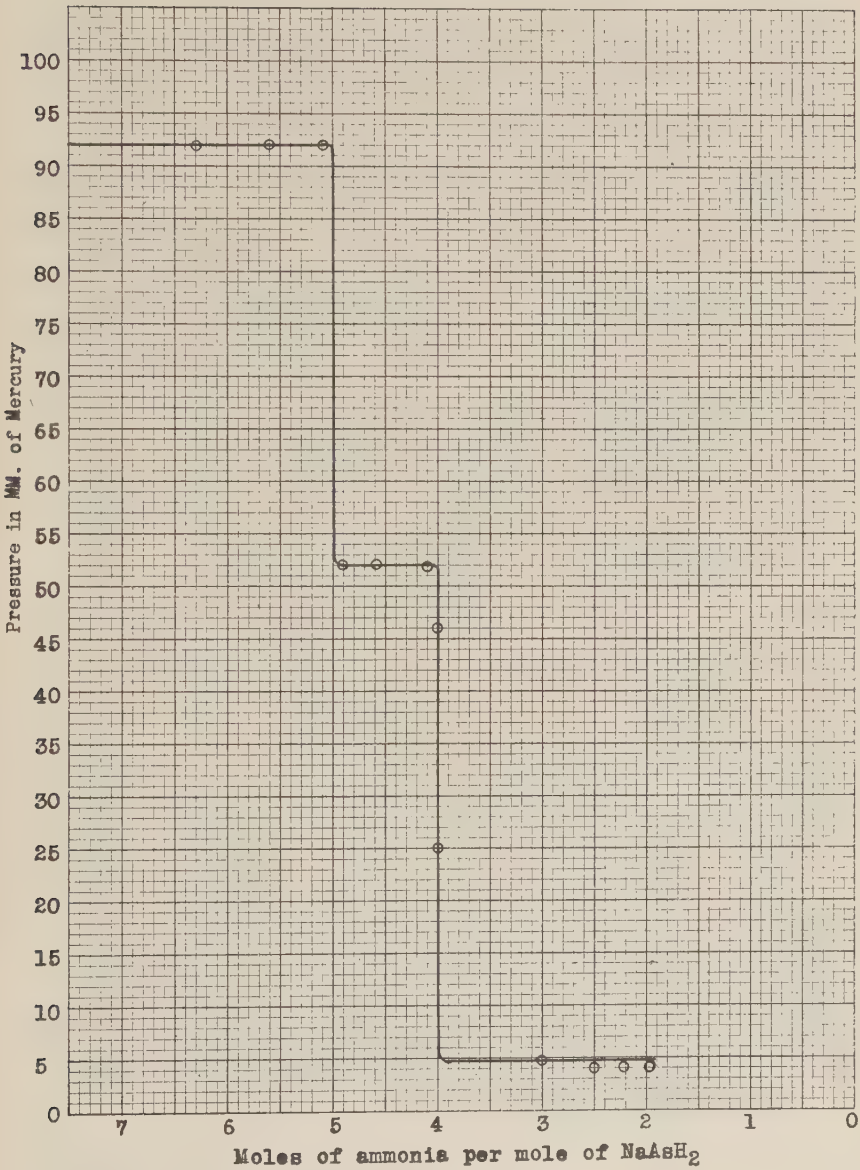

100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
Pressure in MM. of Mercury
7
6
5
4
3
2
1
0
Moles of ammonia per mole of $NaAsH_2$

Fig. 2

When the ammonia-free solid was allowed to warm to room temperature, it darkened rapidly and soon turned into a brownish-black amorphous substance. During the color change hydrogen was evolved, but arsine could not be detected in the gaseous decomposition products. After the substance had remained for several days at room temperature, 80-90% of the available hydrogen had been liberated. The remaining black residue was identical with that obtained by carrying out the preparation at room temperature and pumping off all the ammonia. As already stated in connection with the earlier experiment, a very small quantity of ammonia caused the black residue to turn reddish. This change was undoubtedly due to incomplete decomposition of the dihydrogen arsenide, because no such color change was observed when all of the available hydrogen had been removed. The nature of the decomposition product will be discussed later.

When the compound, $NaAsH_2$-$4NH_3$, was warmed up to 0° C. there occurred a transition from the white crystalline solid to a reddish heterogeneous mixture with solid and liquid phases. Immediately after this change had taken place no hydrogen could be detected in the vapor phase; but after the product had stood for several hours a slow evolution of hydrogen was observed. Vapor pressure measurements on this material were very similar to those made on similar substances prepared at 0° C. No plateau at constant pressure was found, and as ammonia was withdrawn, the rate of hydrogen evolution increased considerably. The liquid phase is undoubtedly an unstable state, because, when it stood at room temperature for several weeks, it completely disappeared, leaving behind a brownish-black residue.

Since a penta- and a tetra-ammonate of sodium dihydrogen arsenide had been shown to exist at low temperature, it was decided

to measure the temperature coefficients of their respective equilibrium vapor pressures, and to determine from these coefficients some indication of the thermal stability of the compounds in question. The equilibrium equations,

$$(NaAsH_2\text{-}5NH_3) \rightleftharpoons (NaAsH_2\text{-}4NH_3) + NH_3,$$

show that the equilibrium constant, K_p, is equal to the pressure of ammonia above the solid phase. From the expression,

$$\frac{d \text{ Ln } Kp}{d\ T} = \frac{\Delta H}{RT^2} \quad \left(\text{which may be written } \Delta H = -R\frac{d \text{ Ln } Kp}{d\ (1/T)}\right)$$

the value of ΔH may be determined by plotting log Kp (or log P) against 1/T, computing the slope of the line, and multiplying this value by 2.303 R.

In order to hold the system at constant temperature long enough to attain equilibrium vapor pressures several different low temperature baths were employed.

Composition of Bath	Temperature
Carbon dioxide-acetone	-78° C.
Chloroform	-64° C.
Acetoacetic ester	-45° C.
Carbon tetrachloride	-23° C.

Since small amounts of water and impurities greatly affect the temperatures of these baths, an ammonia thermometer was used for all measurements.

The data for the temperature coefficient of the vapor pressure of the penta-ammonate are given in Table 7; the resulting log P - 1/T curve is shown in Fig. 3. The slope of the straight line is -1466 which corresponds to a value of about 6700 calories per mole for the heat of decomposition of $NaAsH_2\text{-}5NH_3$.

Similar data for the tetra-ammonate are tabulated in Table 8. Here, however, it is difficult to determine the equilibrium involved, since in order to investigate the lower ammonates,

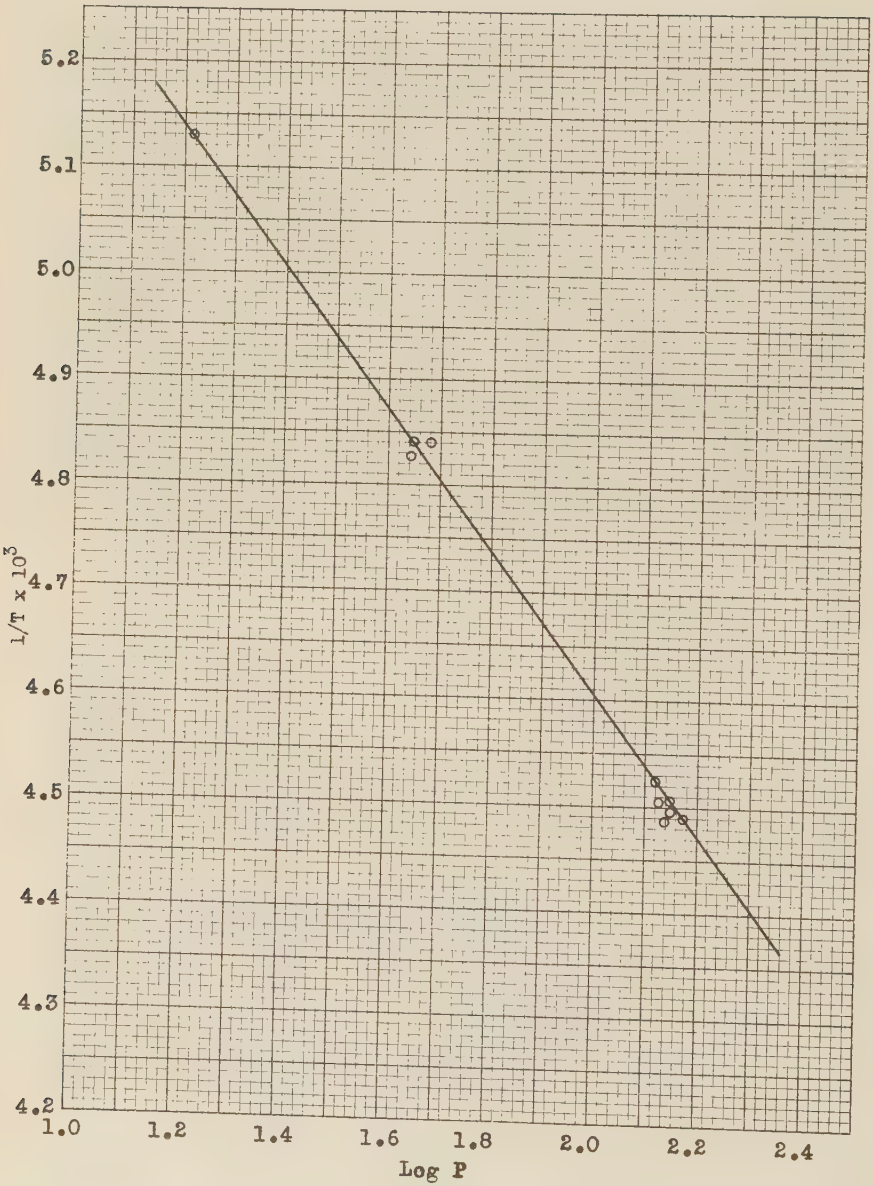


Fig. 3

it was necessary to elevate the temperature; some thermal decomposition consequently occurred. From the experiments in which the degree of ammonation of sodium dihydrogen arsenide was determined by means of weight measurements, it seems probable that the equilibrium equation,

$$(NaAsH_2\text{-}4NH_3) \rightleftharpoons (NaAsH_2\text{-}2NH_3) + 2NH_3,$$

describes the reaction. Here the equilibrium constant, K_p, is equal to the square of the ammonia pressure. The value of ΔH may be obtained by multiplying the value, $-R\frac{d \ln P}{d(1/T)}$, by two. In the plot (Fig. 4) constructed from the data in Table 7 the slope, $\frac{d \ln P}{d(1/T)}$, is -1777; this value applied to the equilibrium in question corresponds to a value of approximately 16,000 calories per mole for the heat of the tetra-ammonate.

TABLE 7

VAPOR PRESSURE OF $NaAsH_2\text{-}5NH_3$ AT VARIOUS TEMPERATURES

Log P	$(1/T) \times 10^3$	Log P	$(1/T) \times 10^3$
1.218	5.131	2.140	4.507
1.653	4.838	2.126	4.525
1.654	4.838	2.148	4.502
1.663	4.836	2.149	4.514
1.658	4.830	2.145	4.514
2.045	4.525	2.151	4.507
2.093	4.545	2.160	4.502
2.097	4.521	2.166	4.500
2.110	4.520	2.164	4.490
3.137	4.507	2.175	4.486

These results seem to agree with qualitative predictions concerning the stability of the ammonates of $NaAsH_2$. The relatively small heats of dissociation of these compounds might be anticipated, for they are completely decomposed at temperatures as low as 0° C. The lower ammonates might, as expected, be somewhat more stable since the polar charge on their cations is distributed among fewer molecules of ammonia.

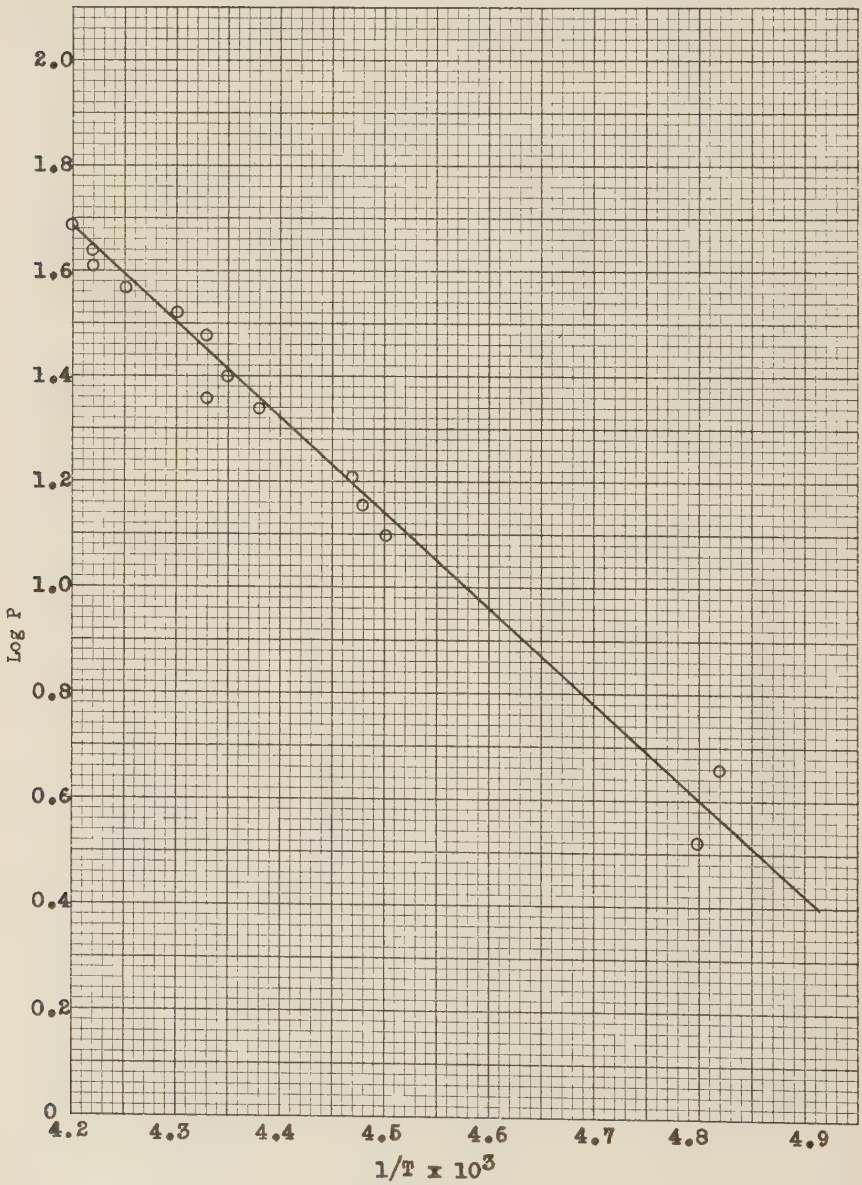


Fig. 4

TABLE 8

VAPOR PRESSURE OF $NaAsH_2$-$4NH_3$ AT VARIOUS TEMPERATURES

Log P	$(1/T) \times 10^3$	Log P	$(1/T) \times 10^3$
0.301	4.840	1.389	4.350
0.477	4.820	1.556	4.260
0.635	4.820	1.628	4.220
0.778	4.780	1.342	4.320
1.114	4.500	1.362	4.320
1.146	4.485	1.633	4.220
1.190	4.475	1.550	4.250
1.332	4.380	1.681	4.200

Thermal Decomposition of Sodium Dihydrogen Arsenide

Sodium dihydrogen arsenide, either in the presence or absense of ammonia, decomposes readily at room temperature, liberating hydrogen and leaving a brownish-black residue. Figure 5 illustrates the rate at which hydrogen is evolved from ammonia-free sodium dihydrogen arsenide at room temperature in vacuo. The change from a white crystalline compound at low temperatures to a black amorphous material at room temperature occurs very rapidly as the material is allowed to warm up. After the hydrogen has been completely removed from the black residue, this material is practically insoluble in liquid ammonia. Some information concerning the nature of the dissociation product may be obtained by treating the material with an acid in liquid ammonia and observing the products formed.

When ammonium chloride in liquid ammonia reacted with the residue about one-third of the available arsenic was liberated as arsine. The remaining two-thirds remained in the form of finely-divided metallic arsenic. Hydrogen was not evolved during the reaction. Table 9 contains the results obtained from the reaction of ammonium chloride in liquid ammonia with the decomposition

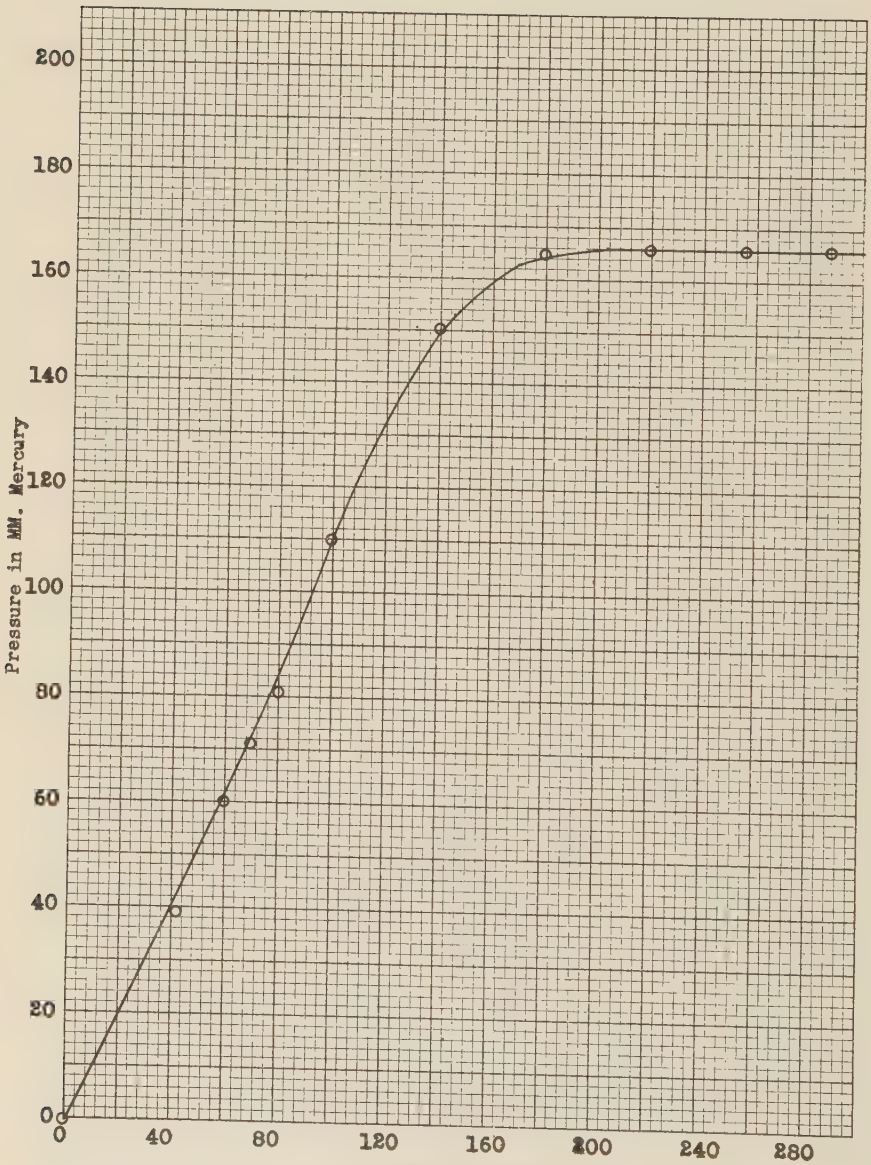

200
180
160
140
120
100
80
60
40
20
0
Pressure in MM. Mercury
0
40
80
120
160
200
240
280
Time in hours

Fig. 5

product of sodium dihydrogen arsenide. Although the experimental data do not agree very well with the predicted values, they serve to distinguish between various possible mechanisms. The volume of arsine liberated was determined by collecting the gas over a dilute sulfuric acid solution. Since arsine is known to be somewhat soluble in such conditions, it is not surprising to find the observed values low.

Any one of the following reactions might possibly represent the thermal dissociation of sodium dihydrogen arsenide.

(1). $3\ NaAsH_2 \longrightarrow Na_3As + 2AsH_3$

(2). $3NaAsH_2 \longrightarrow Na_3As + 2As + 3H_2$

(3). $3NaAsH_2 \longrightarrow Na_3As_3 + 3H_2$

(4). $NaAsH_2 \cdot NH_3 \longrightarrow NaNH_2 + AsH_3$

Reactions 1 and 4 may be discarded since no arsine could be detected in the products resulting from the thermal decomposition of sodium dihydrogen arsenide either in the presence or absence of ammonia. Another reason why reaction 1 is untenable, is that in this reaction subsequent treatment of Na_3As with ammonium chloride in liquid ammonia would eliminate all of the arsenic as arsine, whereas in the experiments approximately two-thirds of the arsenic was deposited in the metallic form. The products of reactions 2 and 3 would react with ammonium chloride in liquid ammonia as follows:

$$2As + Na_3As + 3NH_4Cl \longrightarrow 3NaCl + AsH_3 + 3NH_3 + 2As$$

$$Na_3As_3 + 3NH_4Cl \longrightarrow 3NaCl + AsH_3 + 3NH_3 + 2As$$

Since these two reactions have the same end products, they offer no means of distinguishing between the two mechanisms. Zintl[1] formulates the sodium arsenides as polyanionic substances formed

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[1]Zintl, Gobeau, and Dullenkopf, Z. Physik. Chem., 154B, 1 (1931).

by the addition of arsenic to the normal arsenide.

$$Na_3As + 2As \longrightarrow Na_3\left[\overset{\equiv}{As}(As_2)\right]$$

The difference between reactions 2 and 3 is merely a question of the As-(As_2) bonding strength. It seems probable that in the absence of ammonia, the transition $Na_3As_3 \rightarrow Na_3As + 2As$ should take place spontaneously. Na_3As_3-$(NH_3)_x$ is readily soluble in liquid ammonia, (as shown by Zintl's work), but when once deammonated it does not redissolve. This phenomenon is easily explained by assuming that Na_3As_3 decomposes into the two insoluble products, $Na_3As + 2As$. A convincing proof of the structure of the residue resulting from thermal decomposition of sodium dihydrogen arsenide would be difficult to obtain; X-ray examination would probably be necessary to determine sodium-arsenic bond distances.

TABLE 9

TREATMENT OF DECOMPOSITION PRODUCT WITH NH_4Cl

Wt. $(NaAs)_x$	Loss in Wt.	Theor.*	Vol. AsH_3	Theor.
.1836	.096	.081	15	15
.3607	.173	.158	22	30
.3635	----	----	20	31
.4150	----	----	25	32

*Theoretical values determined according to the product obtained from reactions 2 or 3 on page 27.

The Reaction Between Lithium And Arsine in Liquid Ammonia

No study of the reaction between lithium and arsine appears in the literature. Legoux[1] studied the reaction of phosphine with solutions of lithium in liquid ammonia, and found the product to be a white, crystalline ammonate, $LiPH_2$-$4NH_3$.

[1]Legoux, Compt. Rend. 207, 634 (1938).

The reaction between lithium and arsine in liquid ammonia was carried out in exactly the manner described for the analagous reaction with sodium (Cf p. 17). When an amount of arsine sufficient to discharge the blue color of lithium in ammonia had been admitted to the reaction flask, a clear greenish-yellow solution was formed. Table 10 contains the molar proportions of lithium and arsine employed in the experiment, as well as the amount of hydrogen evolved.

TABLE 10

THE REACTION OF ARSINE WITH LITHIUM IN LIQUID AMMONIA

	Moles of Sodium	Moles of Arsine	Hydrogen Evolved	Molar Ratio
Theor.	1.0	1.0	0.5	1 : 1.00 :0.50
	0.00368	0.00360	0.00183	1 : 0.98 :0.49

The molar ratio corresponds very well to the equation:

$$Li + AsH_3 \longrightarrow LiAsH_2 + \tfrac{1}{2}H_2$$

After removal of all hydrogen from the reaction flask, the solvent was withdrawn in measured quantities; vapor pressure measurements were taken while the system was maintained at -65° C. The results of these measurements are shown in Fig. 6.

As the solvent was withdrawn from the reaction vessel, the color and appearance of the solution remained unchanged until the composition was approximately eleven moles of ammonia per mole of lithium dihydrogen arsenide. At this point, a yellowish crystalline material began to crystallize out. When all the liquid phase had disappeared a perfectly white crystalline product remained in the flask. Fig. 6 shows that lithium dihydrogen arsenide exists at low temperatures in the form of penta-, tetra-, and tri-ammonates. During the vapor pressure measurements, tests were

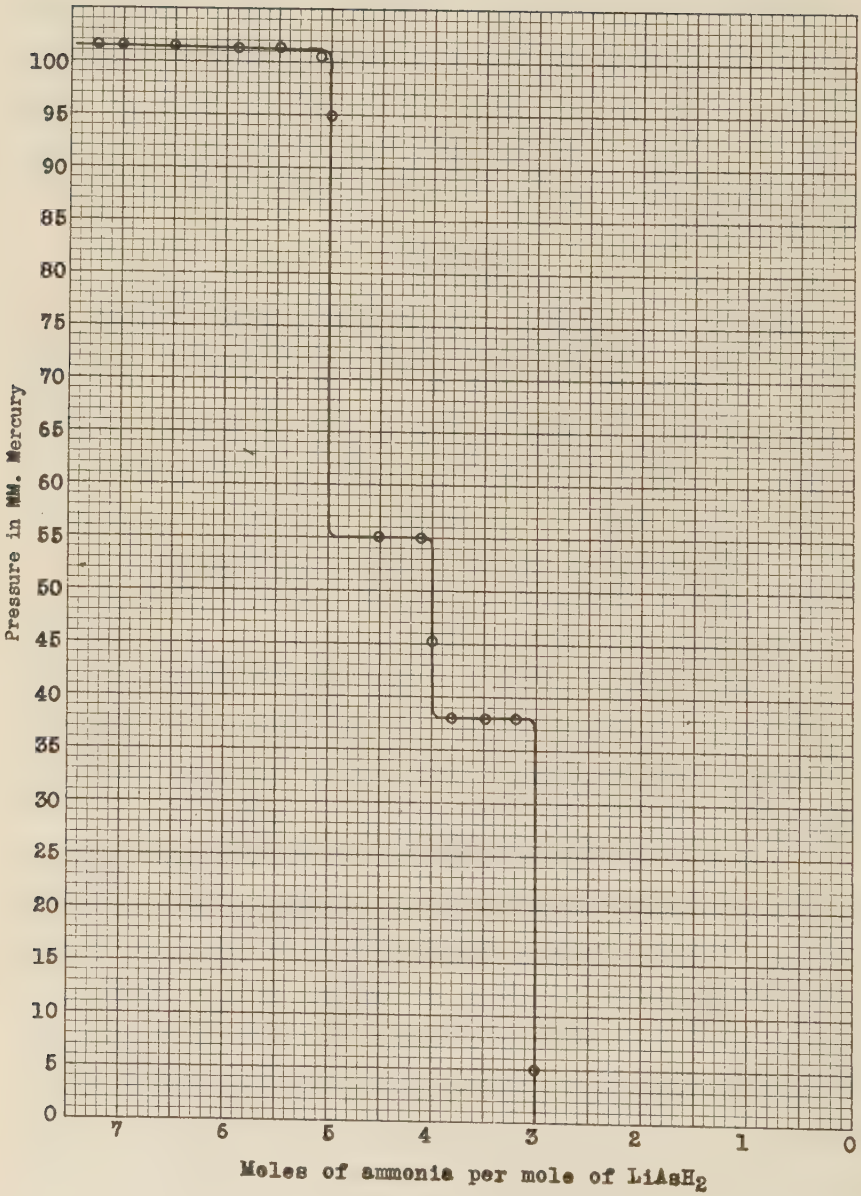
Pressure in MM. Mercury
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
7
6
5
4
3
2
1
0
Moles of ammonia per mole of $LiAsH_2$

Fig. 6

made to detect hydrogen or arsine in the gas pumped off. None was found while the material was kept at low temperatures.

In order to investigate the relative stability of the ammonates of lithium dihydrogen arsenide, the respective temperature coefficients of their vapor pressures were determined. The data are summarized in Tables 11 and 12; the corresponding curves shown in Figs. 7 and 8. For the equilibrium,

$$(LiAsH_2\text{-}5NH_3) \rightleftharpoons (LiAsH_2\text{-}4NH_3) + NH_3,$$

the value of $\frac{dLnP}{d(1/T)}$ is -1486, corresponding approximately to 6800 calories per mole for the heat of dissociation of the penta-ammonate. The tetra-ammonate dissociates similarly according to the equilibrium:

$$(LiAsH_2\text{-}4NH_3) \rightleftharpoons (LiAsH_2\text{-}3NH_3) + NH_3$$

For this reaction the variation with temperature of the ammonia gas pressure above the solid phase is shown in Fig. 8. The slope of the line is -1375, corresponding to 6300 calories per mole for the heat of dissociation.

TABLE 11

TEMPERATURE COEFFICIENTS OF VAPOR PRESSURE FOR THE SYSTEM $(NaAsH_2\text{-}5NH_3) \rightleftharpoons (NaAsH_2\text{-}4NH_3) + (NH_3)$

Log P	$(1/T \times 10^3)$	Log P	$(1/T \times 10^3)$
1.7482	4.840	2.1818	4.535
1.6180	4.890	2.1903	4.531
1.6946	4.862	2.1945	4.527
1.7033	4.857	2.2000	4.525
1.3010	5.131	2.2135	4.515
2.1673	4.527	2.2201	4.501
2.1875	4.519	1.7634	4.845
2.1973	4.515	1.3117	5.110

At a composition of three moles of ammonia per mole of lithium dihydrogen arsenide, the vapor pressure of the ammonate was too low to be measured conveniently at the low temperatures. When the temperature was raised to 0° C. the material appeared to

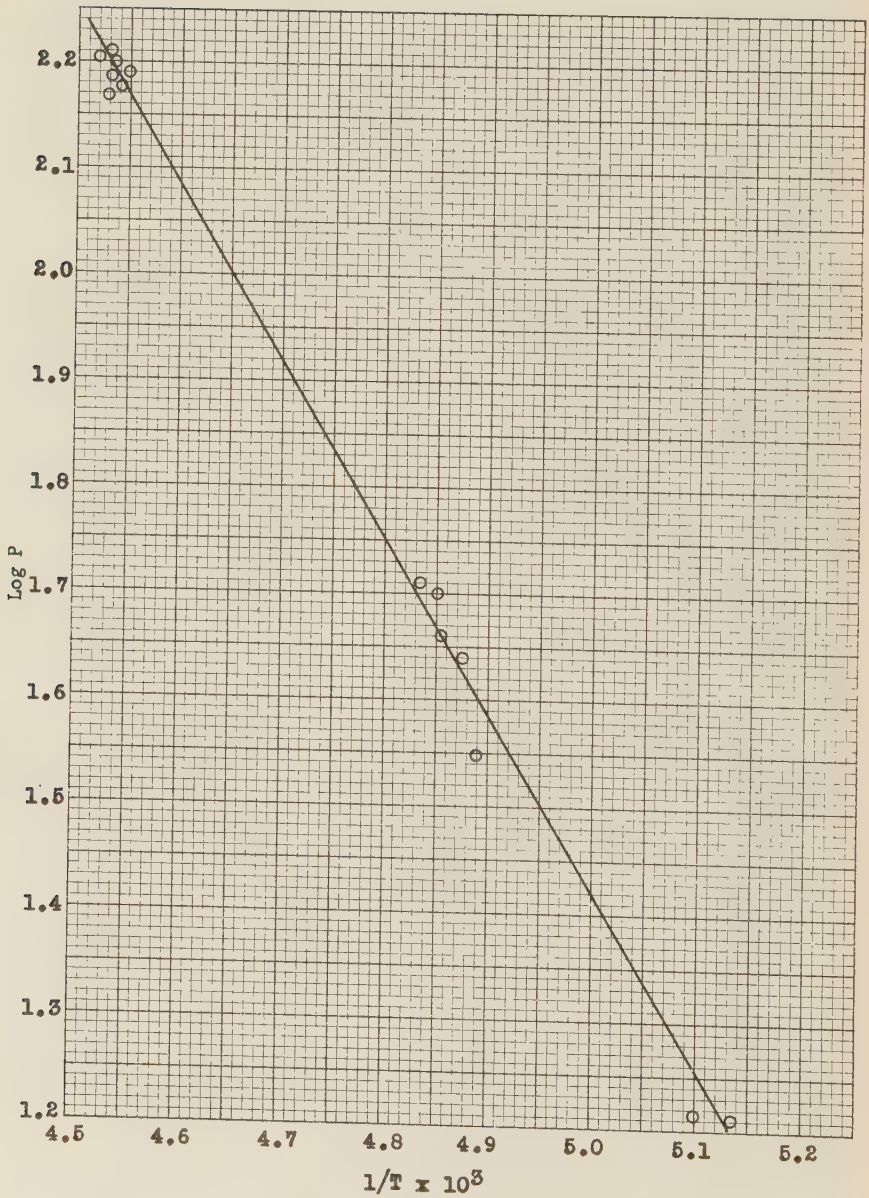

Fig. 7

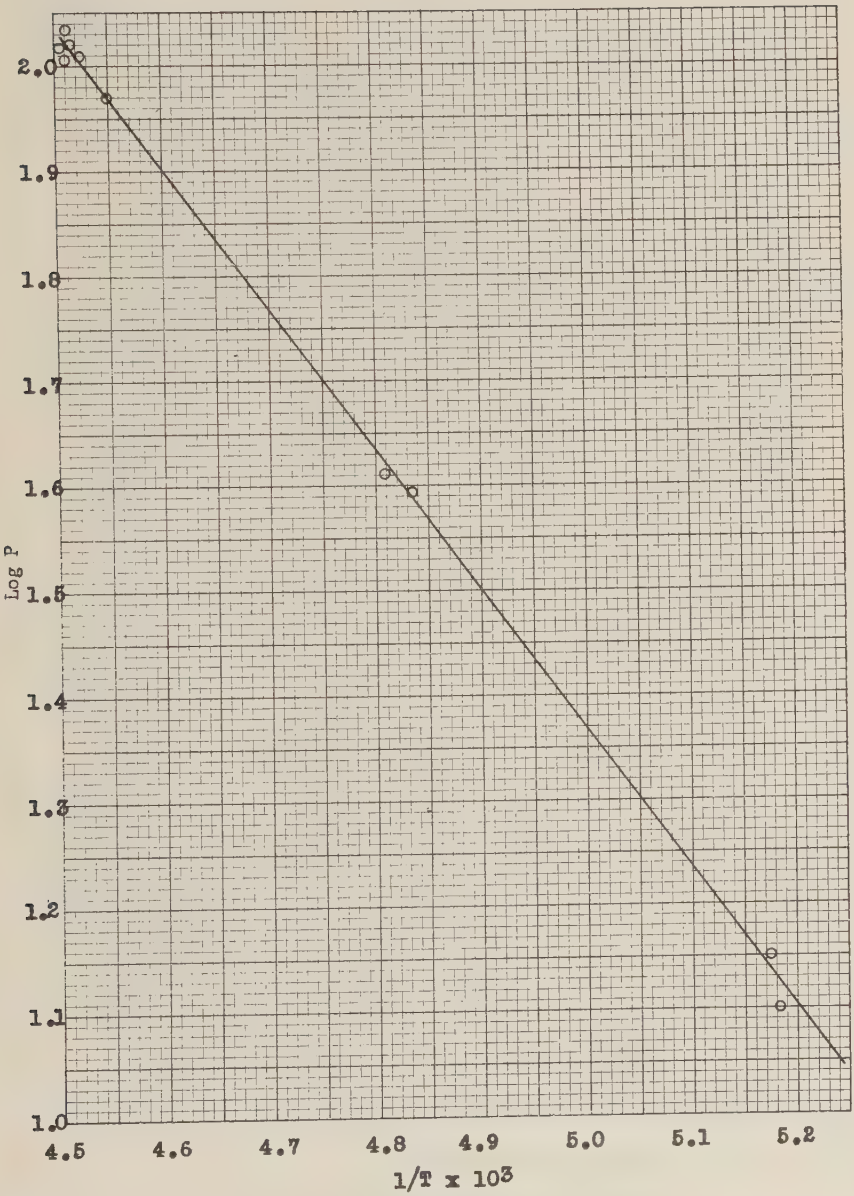

Fig. 8

be stable; the pressure of ammonia gas above the solid was 36 mm. However, after standing for ten hours, the white crystalline substance changed to a dull gray amorphous material. When the temperature was further elevated to 25° C., the pressure of ammonia above the solid residue increased to 106 mm. and remained fairly constant at that value until the composition became approximately one mole of ammonia per mole of the arsenide.

TABLE 12

TEMPERATURE COEFFICIENT OF VAPOR PRESSURE FOR THE SYSTEM $(NaAsH_2 - 4NH_3) \rightleftharpoons (NaAsH_2 - 3NH_3) + (NH_3)$

Log P	$(1/T \times 10^3)$	Log P	$(1/T \times 10^3)$
1.5846	4.836	2.0434	4.501
1.6075	4.810	2.0354	4.513
1.1761	5.141	2.0374	4.507
1.9934	4.535	1.1461	5.139
2.0334	4.509		

During the time in which vapor pressure measurements at room temperature were taken, the material darkened and began slowly to liberate hydrogen. The thermal decomposition of the lithium compound differed from that of the corresponding sodium compound in that not only hydrogen but also a small amount of arsine was evolved. The initial and final weights of the reaction flask plus products show that only a very small proportion of the available arsenic was lost as arsine during thermal decomposition. The formation of arsine may be explained by assuming an ammonolytic reaction, $LiAsH_2\text{-}NH_3 \longrightarrow LiNH_2 + AsH_3$. Or perhaps there is some tendency for the lithium compound to form an arsenimide,

$$2\ LiAsH_2 \longrightarrow Li_2AsH + AsH_3.$$

The predominant reaction, however, seems to involve the loss of hydrogen, and may be represented by the equation:

$$3LiAsH_2 \longrightarrow Li_3As + 2As + 3H_2.$$

Actually about 50% of the available hydrogen was liberated at room temperature. The solid residue assumed an appearance very much like that of the thermal decomposition product of sodium dihydrogen arsenide.

The Reaction Between Arsine and Calcium in Liquid Ammonia

Lebeau[1] allowed arsine to react with a solution of calcium in liquid ammonia and concluded that the product of the reaction was Ca_3As_2-$AsH_3(NH_3)_x$. After he had distilled off the solvent and heated the product in vacuo to 150° C., he identified the final material as Ca_3As_2. Apparently, there has been no further investigation of this particular reaction.

In a recent article, Legoux[2] described the reaction between phosphine and solutions of calcium in liquid ammonia. He found that the product, unlike the corresponding phosphides of lithium, sodium, and potassium, was quite insoluble in liquid ammonia. The composition of the calcium salt corresponded to the formula $Ca(PH_2)_2$; this salt existed as either a hexa- or di-ammonate at 0° C.

In the present investigation arsine was bubbled slowly into a solution of known amounts of calcium in ammonia maintained at -80° C. The formation of a white insoluble precipitate by the initial addition of arsine indicated that the product was very slightly soluble in liquid ammonia. As soon as the blue color of the solution had been discharged, the amount of the arsine employed was computed and the volume of the hydrogen measured in the usual manner. The results obtained are listed in the following table. (Theoretical values refer to a reaction yielding $Ca(AsH_2)_2$).

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[1]Lebeau, Ann. Chim. Phys. 25, 470 (1902).

[2]Legoux, Compt. Rend., 209, 47 (1939).

TABLE 13

THE REACTION BETWEEN ARSINE AND CALCIUM IN LIQUID AMMONIA

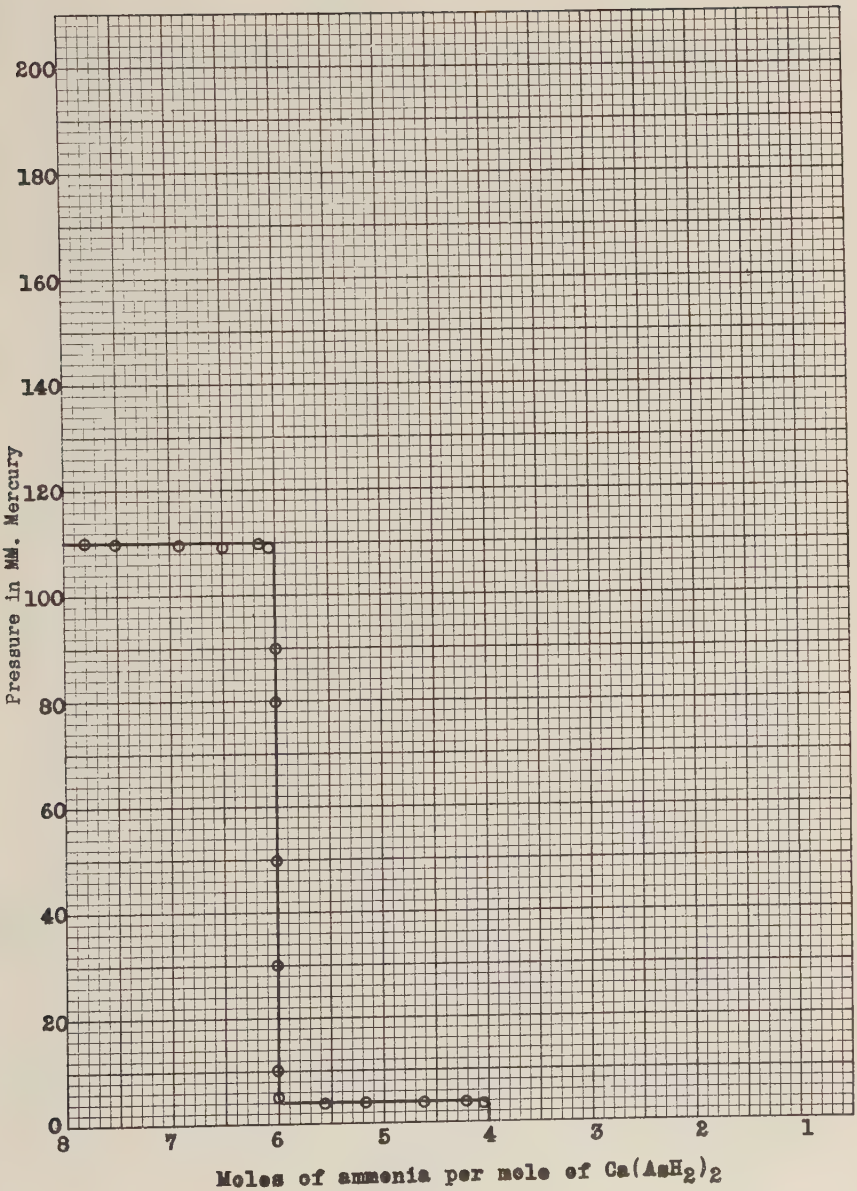
	Moles of Calcium	Moles of Arsine	Moles of H_2 Evolved	Molar Ratio
Theor.	1.0	2.0	1.0	1 : 2.00 :1.00
	0.001987	0.003982	0.001962	1 : 2.01 :0.98

According to these results the product is $Ca(AsH_2)_2$ rather than Ca_3As_2-AsH_3, which would require a molar ratio of 1.0 calcium; 1.0 arsine; 1.0 hydrogen (evolved). When the reaction was complete there remained an insoluble white crystalline residue beneath a clear yellow supernatant liquid. Here again the AsH_2^- ion appears to impart a yellow color to solutions of liquid ammonia.

Ammonia gas was withdrawn from the system in measured quantities while the reaction flask was maintained at -65° C. The solubility of the material in liquid ammonia was so low that the vapor pressure of ammonia above the solution did not differ by a measurable amount from that of pure ammonia. At a composition corresponding to six moles of ammonia per mole of arsenide, the vapor pressure decreased abruptly from 110 mm. to 4 mm. Upon continued withdrawal of ammonia, the pressure remained constant until a composition corresponding to four moles of ammonia per mole of arsenide was attained; at this point the vapor pressure dropped to a value too low to be measured by means of a manometer. The results obtained by measuring the vapor pressure of the system at -65° C. while ammonia gas was being withdrawn are shown in Fig. 9.

The vapor pressure of ammonia gas above the system, represented by the equilibrium equation,

$$(Ca(AsH_2)_2\text{-}6NH_3) \rightleftharpoons (Ca(AsH_2)_2\text{-}4NH_3) + 2NH_3,$$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Pressure in MM. Mercury
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1
Moles of ammonia per mole of $Ca(AsH_2)_2$

Fig. 9

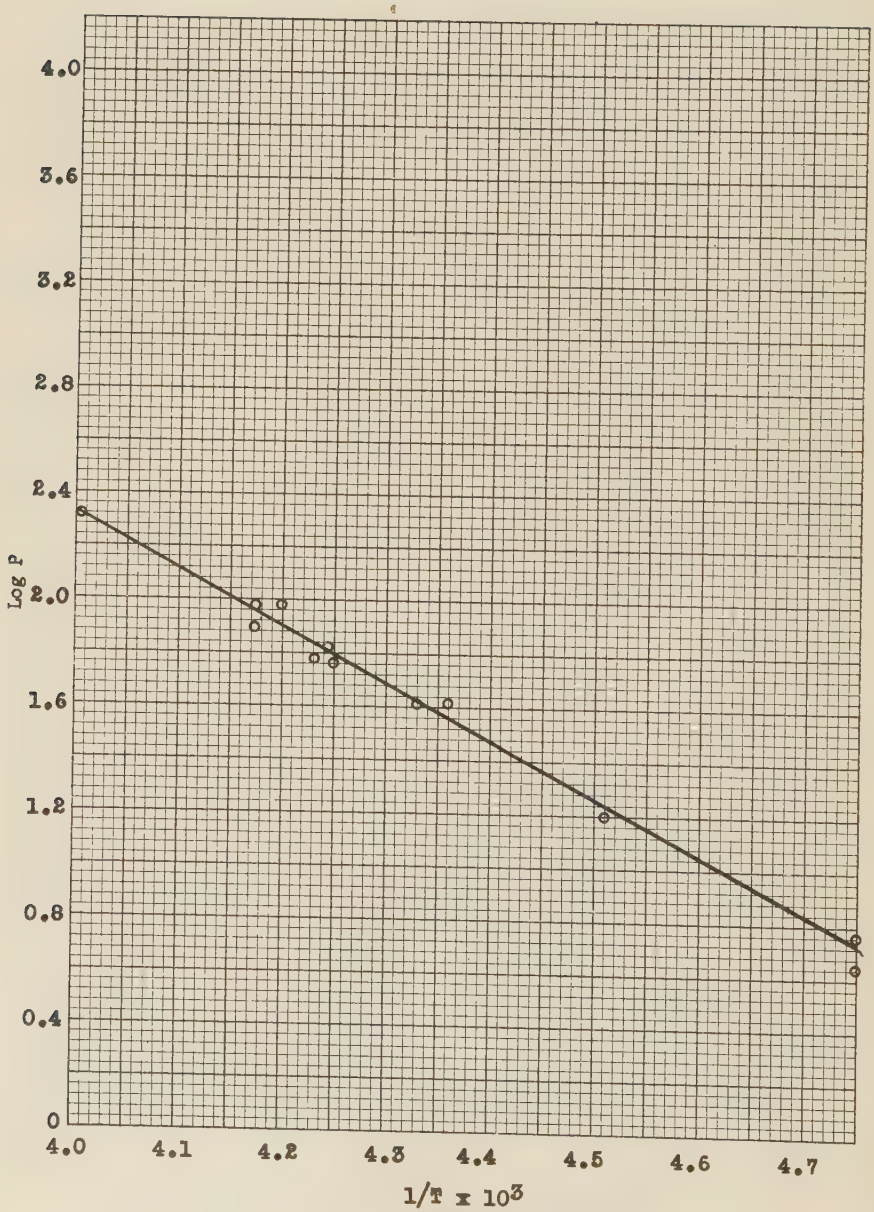

Fig. 10

was determined at several different temperatures. The data are tabulated in Table 14; the corresponding plot is shown in Fig. 10. The slope of the line, $\frac{dLnP}{d(1/T)}$, is -2175, corresponding to an approximate value of 20,000 calories per mole for the heat of dissociation of the hexa-ammonate.

TABLE 14

TEMPERATURE COEFFICIENT OF VAPOR PRESSURE FOR THE SYSTEM:
$(Ca(AsH_2)_2\text{-}6NH_3) \rightleftharpoons (Ca(AsH_2)_2\text{-}4NH_3) + 2NH_3$

Log P	$(1/T \times 10^3)$	Log P	$(1/T \times 10^3)$
2.332	4.00	0.602	4.78
0.699	4.81	0.699	4.78
1.041	4.59	1.813	4.24
1.243	4.51	1.816	4.24
1.643	4.37	1.914	4.19
1.638	4.32	1.949	4.17

When a sample of calcium dihydrogen arsenide tetra-ammonate was warmed to room temperature it underwent a series of color changes. The white crystalline material became yellow, then light brown, and (after standing for several hours) a finely-divided black powder. While this color change was taking place, small amounts of hydrogen and arsine were liberated from the solid; vapor pressure measurements of ammonia gas in the system, therefore, became quite erratic. However, it seems fairly certain that no ammonates lower than the tetra-ammonate exist. The samples of gas withdrawn from the system were first cooled in a liquid nitrogen bath; next the volume of non-condensible gas (hydrogen) was measured; finally, the hydrogen was removed by means of the vacuum pump. The molecular weight of condensible gases was found to vary from 19.0 to 22.4--figures which indicate appreciable amounts of arsine in the ammonia removed. Finally, the material in the reaction flask was subjected to temperatures up to 150° C. for

several hours, until there was no evidence of further gas evolution. After the reaction flask had been evacuated it was weighed; the weight of the residue was found to be 0.3347 gm. as compared to 0.3850 gm., the calculated weight of $Ca(AsH_2)_2$. The 0.05 gm. loss in weight corresponds very closely to the amount of arsine lost from the system during thermal decomposition--approximately 20 cc. of gas measured under standard conditions.

The black residue resulting from thermal decomposition of calcium dihydrogen arsenide was completely insoluble in liquid ammonia. When ammonium chloride was added to the suspension of insoluble material in liquid ammonia, a small amount of gas was slowly liberated; this gas was collected over water. During the reaction the black residue changed to a reddish-brown.

During the thermal decomposition of calcium dihydrogen arsenide, approximately one-fourth of the available arsenic was liberated as arsine, and about one-half of the available hydrogen was given off. These facts indicate that the mechanism of the process may involve the two following equations:

$$(1).\quad Ca(AsH_2)_2 \longrightarrow CaAsH + AsH_3$$

$$(2).\quad Ca(AsH_2)_2 \longrightarrow CaAs_2 + 2H_2$$

Reaction (1) shows the formation of an arsenimide with the simultaneous loss of one molecule of arsine. If this reaction comprised one-half of the total process, 25 cc. of arsine would have been liberated. The volume actually found was very close to that amount. Reaction (2) involves the formation of a "polyarsenide" of calcium, which would undoubtedly be unstable with respect to further decomposition into Ca_3As_2 and arsenic. This secondary dissociation may have been largely responsible for the color changes observed; Ca_3As_2 is red; finely divided arsenic is black. The volume of hydrogen evolved in the thermal decomposition was approximately

that calculated if reaction (2) is assumed to constitute one-half of the total process. The products of both reactions (1) and (2) would be expected finally to form Ca_3As_2 when drastically heated. When Lebeau heated the reaction product of arsine and solutions of calcium in liquid ammonia, the fact that arsine was liberated and that Ca_3As_2 remained as the final product undoubtedly led him to ascribe to the material a composition corresponding to Ca_3As_2-AsH_3 (Cf. p.35). The conditions of his experiment would not have enabled him to isolate the salt $Ca(AsH_2)_2$; apparently, he obtained only its decomposition products.

The products of reactions (1) and (2) might be expected to react with ammonium chloride in liquid ammonia according to the following equations:

$$(3).\quad CaAsH + 2NH_4Cl \longrightarrow CaCl_2 + 2NH_3 + AsH_3$$

$$(4).\quad CaAs_2 + 2NH_4Cl \longrightarrow CaCl_2 + 2NH_3 + As_2H_2$$

The loss in weight of the material described on p. 40 when treated with ammonium chloride in liquid ammonia was 0.1425 gm. This value corresponds to the loss in weight that would occur if reactions (3) and (4) contributed equally to the total reaction. This agreement may be fortuitous because the decomposition of calcium dihydrogen arsenide undoubtedly involves the occurrence of several simultaneous reactions and a complete description of the process would require a more extended study of this particular subject.

The Reaction Between Arsine and Solutions of Potassium in Liquid Ammonia

A description of the preparation and discussion of the properties of potassium dihydrogen arsenide may be found in an article by Johnson and Pechukas.[1] In the present investigation the system, $KAsH_2$-NH_3, was studied at low temperatures to determine whether or not stable ammonates of the salt exist.

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[1]Johnson and Pechukas, J. A. C. S., 59, 2068 (1937).

Potassium dihydrogen arsenide was prepared in the usual manner by bubbling arsine into solutions of potassium in liquid ammonia until the blue color of the metal was discharged. The results of preparations of the material were in complete accord with those of the article mentioned above.

The potassium salt is extremely soluble in liquid ammonia. Withdrawal of ammonia from a dilute solution of $KAsH_2$ in liquid ammonia at -65° C. progressively lowers the vapor pressure of the solvent until a composition of approximately four moles of ammonia per mole of salt is attained, at which point crystallization occurs. The equilibrium expressed by the equation,

$$\text{Sat'd. Sol'n. of } KAsH_2 \text{ in } NH_3 \rightleftharpoons KAsH_2(s) + NH_3(l),$$

takes place at constant pressure (35 mm. at -65° C.) until all ammonia has been withdrawn from the system. From this the interesting conclusion may be drawn that potassium dihydrogen arsenide does not form stable crystalline ammonates even at temperatures as low as -65° C. Figure 11 shows the results of vapor pressure-composition measurements for the system $KAsH_2$-NH_3. This curve differs remarkably from those representing similar systems with other compounds of the type $MAsH_2$, in that such a pronounced lowering of the vapor pressure of the solvent is observed.

Discussion of Results

Arsine reacts with solutions of alkali and alkaline earth metals in liquid ammonia to form salts of the types $MAsH_2$ and $M(AsH_2)_2$ respectively. The chemical composition and general appearance of these salts are identical with those of the corresponding potassium salt described by Johnson and Pechukas.[1] The sodium, lithium, and calcium arsenamides are much less stable

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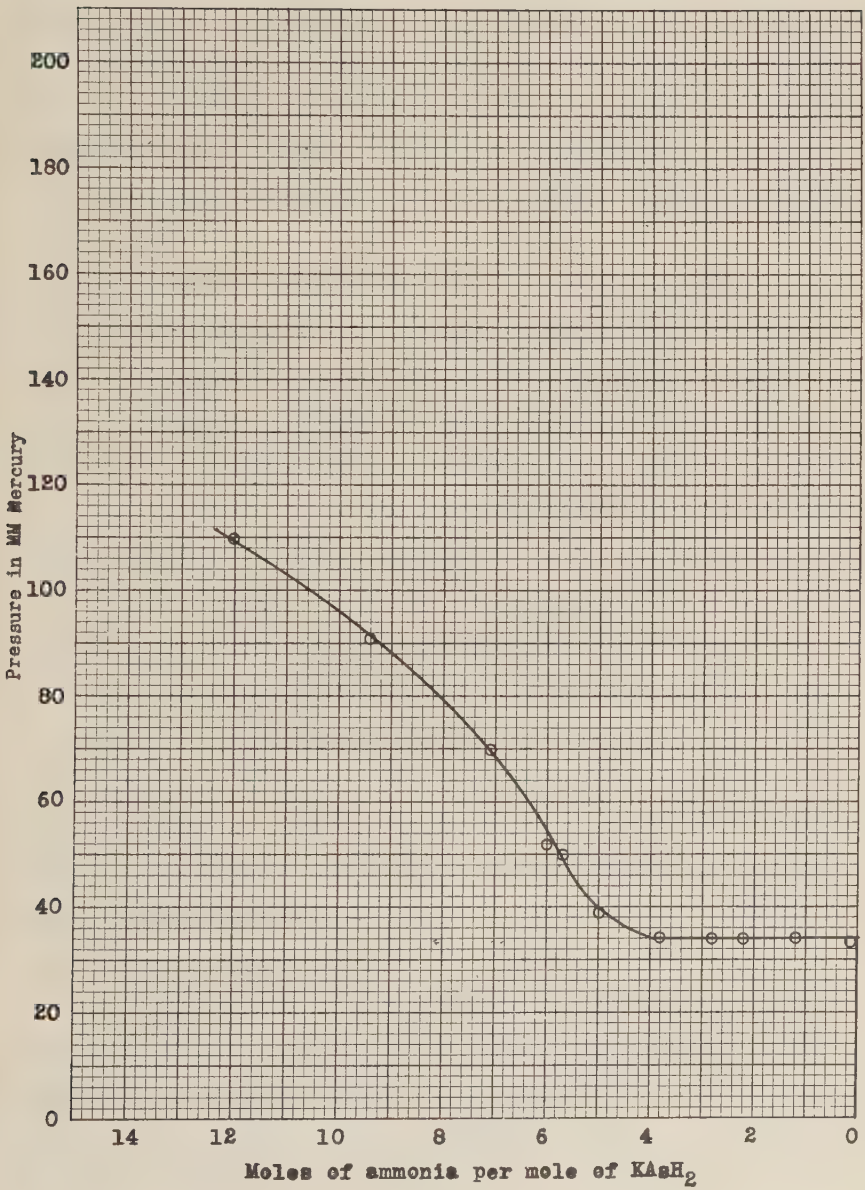
[1]Johnson and Pechukas, J. A. C. S., 59, 2068 (1937).


200
180
160
140
120
100
80
60
40
20
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Pressure in MM Mercury
14
12
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8
6
4
2
0
Moles of ammonia per mole of $KAsH_2$

Fig. 11

thermally than the potassium arsenamide. It was necessary to prepare the former compounds at low temperatures; otherwise a complex mixture of decomposition products was formed. The arsenamides, when prepared and maintained at low temperatures, are well-defined white crystalline salts. Lithium, sodium, and potassium arsenamides are very soluble in liquid ammonia; the solutions are bright yellow. Calcium arsenamide, however, is only slightly soluble in liquid ammonia; the solution above the insoluble residue is light yellow.

The alkali and alkaline earth metal arsenamides with the exception of potassium, when prepared at low temperatures in liquid ammonia solutions, exist in the form of ammonates. In the crystalline state the sodium and lithium salts possess as a maximum five molecules of solvated ammonia, whereas the calcium salt possesses six. These ammonates are all quite stable and may be converted reversibly to lower ammonates provided the temperature is kept below the decomposition point of the arsenamides.

Cation size has an important effect on the stability of compounds of the type, $MAsH_2$. Potassium arsenamide is quite stable at room temperature. Thermal decomposition of this compound at higher temperatures (125 - 150° C.) results in the liberation of all the available hydrogen. Sodium arsenamide, when prepared and maintained at low temperatures, resembles the potassium compound. This sodium salt, however, is unstable at temperatures as low as 0° C.; it dissociates quite rapidly at room temperature, evolving approximately 90% of the theoretical volume of hydrogen. The corresponding lithium and calcium salts are also unstable at 0° C. These latter salts, when allowed to decompose slowly at 0° C. change in appearance just as does the sodium salt. The white crystalline salts gradually darken and ultimately assume

the form of finely-divided black powders. Calcium and lithium arsenamides differ from the corresponding potassium and sodium compounds, however, in that they evolve arsine as well as hydrogen during their thermal dissociation. The most stable compounds of the arsenamide type should be those with cations of large ionic radii. Thus cesium and rubidium arsenamides should be even more stable than the potassium compound. On the other hand, metals with small ionic radii, such as zinc, probably form very unstable salts of arsine.

It was originally believed that in metals with a large value for the ratio, ionic radius/ionic charge, the effective cation size might be increased by the greater tendency to solvation. The results obtained were not well-enough defined to confirm this postulate. However, the calcium and lithium arsenamides in the presence of ammonia decomposed somewhat more slowly than did the corresponding sodium compound. When an ammonate of sodium arsenamide was allowed to warm up to 0° C. the material underwent a profound color change and a liquid phase was formed. Under similar conditions lithium and calcium arsenamides formed no liquid phase. These observations probably indicate that in the crystalline calcium and lithium salts, ammonia is bound more firmly than it is in the sodium salt. Apparently in none of the ammonates of the alkali or alkaline earth metal arsenamides is the ammonia bound firmly enough to increase effectively the stability of the crystalline compounds.

An effort was made to determine the mechanism of the thermal dissociation of the arsenamides. Sodium arsenamide decomposes at room temperature, liberating hydrogen, and leaving a black residue. This reaction proceeds according to one of the two following equations:

(1). $3NaAsH_2 \longrightarrow Na_3As + 2As + 3H_2$

(2). $3NaAsH_2 \longrightarrow Na_3As_3 + 3H_2$

Since no means of distinguishing between these two reactions has been found, it has been impossible to reach definite conclusions regarding the nature of the decomposition product. The products of reaction (1) may be regarded as the final substances derived by the successive loss of two molecules of arsine from the original sodium arsenamide, with simultaneous dissociation of the evolved arsine into its elements.

(a). $2NaAsH_2 \rightarrow Na_2AsH + AsH_3$

(b). $3Na_2AsH \rightarrow 2Na_3As + AsH_3$

It seems certain that the thermal decomposition of the corresponding lithium and calcium compounds proceeds, at least partially, according to mechanisms similar to (a) and (b). Another analogy which seems to support this type of mechanism, is that lithium amide dissociates thermally forming by successive loss of ammonia first an imide and finally a nitride.

Lithium and calcium arsenamides decompose thermally evolving a mixture of hydrogen and arsine. This fact probably indicates that the products formed by loss of arsine are first an arsenimide and finally an arsenide. If this hypothesis is correct it is difficult to explain why arsine is obtained in the decomposition of lithium and calcium arsenamides but not in the decomposition of the sodium or potassium compounds. This same difference occurs in the corresponding series of amides. Sodium and potassium amides dissociate into their elements when heated to high temperatures. Lithium and calcium amides, on the other hand, lose ammonia and form both imides and nitrides. Other amides (such as those of zinc, barium, and germanium) when heated, form either imides, nitrides, or both; there is a simultaneous loss of ammonia. Alkali

and alkaline earth metal hydrogen phosphides of the type, MPH_2, decompose, liberating phosphine and forming normal phosphides.

It seems unreasonable to believe that when sodium and lithium amides are subjected to thermal dissociation, the difference in their behaviour is one of kind rather than of degree. A thorough investigation of the mechanisms of thermal decomposition of the alkali and alkaline earth metal amides would permit an excellent correlation of the facts concerning amide type compounds of the fifth group elements. The influence of the cation on the thermal dissociation process of the amides and related compounds is not very well understood at the present time. This effect may very well agree with Zintl's idea about the stability of polyanionic substances (Cf. p. 5), but the evidence on this point available at the present does not warrant definite conclusions.